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MECHANISM AND KINETICS OF THERMAL DECOMPOSITION OF PRECIPITATES OF THE ZINC OXIDE–ALUMINIUM OXIDE SYSTEM FROM NON-ISOTHERMAL TG CURVES

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ABSTRACT

Kinetics of decomposition of the precipitates of the ZnO–Al_2O_3 system, prepared by coprecipitation and mechanical mixing of the individual precipitates, have been studied. The decomposition of zinc basic carbonate is a first order rate process with an activation energy of 34.5 kcal/mole (Coats and Redfern equation). The decomposition of aluminium hydroxide is also best described as a first order rate process with one break in the Coats and Redfern plot corresponding to activation energies of 29.4 and 8.3 kcal/mole respectively. The entire course of decomposition of coprecipitated as well as mechanically mixed samples cannot be described by any one of the many rate equations available. Consequently, the Coats and Redfern equation has been employed. The plots indicate one or two breaks and thus two to three values of activation energy are reported. From the results it is to be concluded that decomposition of these precipitates is a heterogeneous process. The first step is definitely the decomposition of zinc basic carbonate followed by decomposition of aluminium hydroxide and/or interaction of the two precipitates resulting in the formation of "precursor" to spinel. The results of our earlier investigation on the same system (especially the formation of precursors) are well supported by the results reported in this investigation.

A new equation (a modified form of the Elovich equation) has been proposed for such heterogeneous decomposition processes. The proposed equation also appears to be the general form of the equations where diffusion is the rate controlling process.

INTRODUCTION

Kinetic studies on the thermal decomposition of mixed systems have scarcely been attempted due to obvious complexities involved in the interpretation of thermogravimetric data and also in arriving at a suitable rate equation and rate controlling processes. These difficulties are further accentuated by the limited applicability of various derivations used for obtaining kinetic parameters from nonisothermal thermogravimetric curves. In an earlier communication[1] on the ZnO–Al_2O_3 system, the composition of the precipitates and decomposition products were ascertained by chemical, thermogravimetric (TG) and differential thermal analysis (DTA) methods. While comparing DTA peaks with TG results, it was observed that a new peak appears around 275 °C in the DTA curves of some of the coprecipitated and mechanically mixed samples, which has been attributed to a solid state reaction between the two components, resulting in the formation of a precursor to spinel, $2ZnO \cdot 3Al_2O_3$. A peak at this temperature is absent in the corresponding pure components. It is of interest to study how this reaction manifests itself in the kinetic treatment of the data and also the kinetics and mechanism of this interaction.

EXPERIMENTAL

The experimental details have already been described in an earlier paper[1].

RESULTS AND DISCUSSION

The fraction decomposed versus temperature plots for coprecipitated and mixed samples are given in ref. 1. For the coprecipitated samples the curves are fairly smooth. In the case of mechanical mixtures distinct breaks are observed which approximately correspond to the various proportions of ZnO and Al_2O_3 in the mixtures.

Most of the dehydration reactions and pyrolytic decomposition have been assumed to be of first order[2]. The Freeman and Carroll[3] equation,

$$\frac{-E/2.3\,R\,\Delta T^{-1}}{\log Wr} = -x + \frac{\log (\mathrm{d}W/\mathrm{d}t)}{\log Wr} \tag{1}$$

for the estimation of E (activation energy) and x (order of reaction), though it has been very widely used, seems to suffer from several disadvantages[4]. Our experience regarding the application of this equation in ZnO–Al_2O_3 samples further exposes its limitations. For pure components (aluminium hydroxide and zinc basic carbonate) as well as their mixtures, the plots are not straight lines, and regression analysis of the highly scattered points gives in most cases a negative value for the order of reaction which has no significance. It is quite possible that this may be due to the complexity of the reaction itself and not due to the inherent nature of the derivation.

Šatava[5,6] recently proposed a simplified graphical method based on the assumption that the non-isothermal experiment proceeds in an infinitesimal time interval, isothermally, so that the rate can be described by equation

$$\mathrm{d}\alpha/\mathrm{d}t = Ze^{-E/RT}f(\alpha) \tag{2}$$

where α is fraction decomposed in time t, $f(\alpha)$ depends on the mechanism of the process, E is the activation energy and Z is the pre-exponential factor. In the case of a constant temperature increase, $\mathrm{d}T/\mathrm{d}t = q$, the integration of eqn (2) leads to the new functions, g(α) and p(x)

$$\frac{d(\alpha)}{f(\alpha)} = g(\alpha) = \frac{E}{Rq} \cdot p(x). \tag{3}$$

For the correct mechanism log [g(α)] should be a linear function of $1/T$.

From the various rate equations (ref. 5, Table 1), the plots of log [g(α)] versus $1/T$ for the pure components (1A and 1B), representative coprecipitated (1D and 1E) and mixed sample (2E) of the ZnO–Al_2O_3 system, are shown in Figs. 1–5. It can be seen that for pure zinc basic carbonate and aluminium hydroxide, a first order (F1) rate equation gives a near straight line. For the coprecipitated and mixed samples, out of nine equations for which log [g(α)] values have been plotted, no single equation seems to satisfy the entire experimental data. A sort of regularity is observed in the curves; the deviation starting from a straight line (for eqn F1 for example in pure zinc basic carbonate) increases with increasing percentage of aluminium

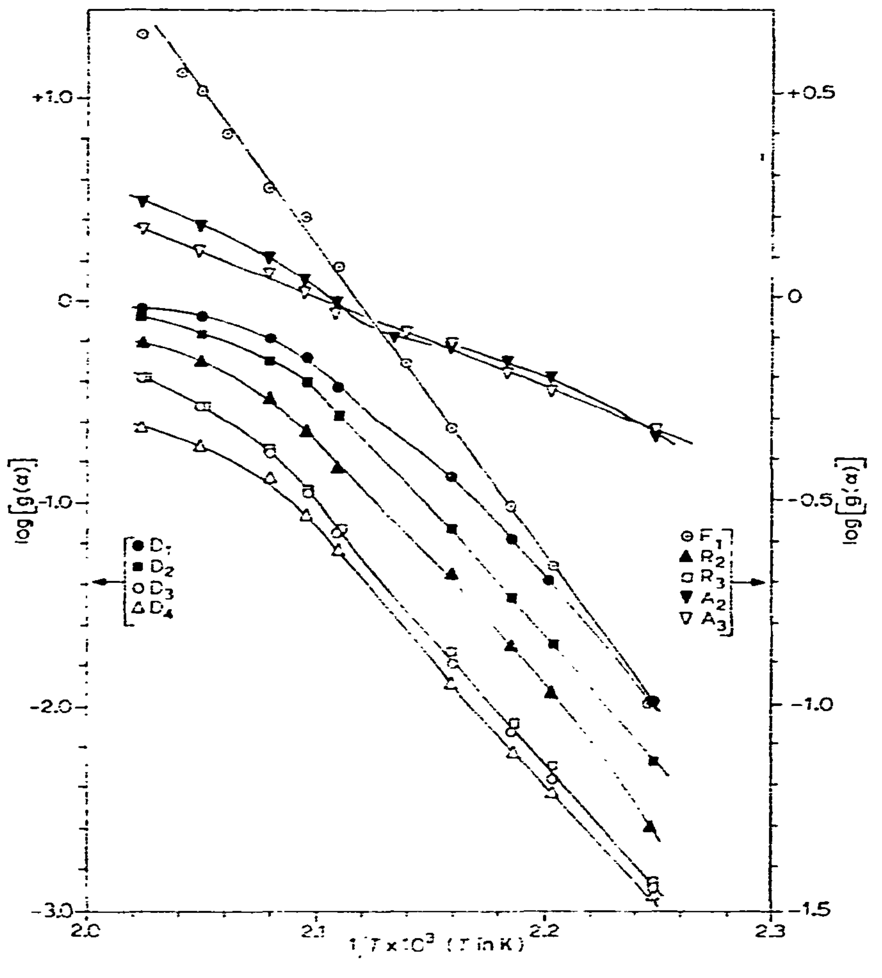

Fig. 1. Šatava's plot for zinc basic carbonate (sample 1A).

hydroxide. Therefore, from the curves, it is almost impossible to select the exact mechanism or the rate equation which may be applicable in coprecipitated ZnO–Al_2O_3 samples. Another important observation which can be made from the nature of log [g(α)] versus $1/T$ plots of coprecipitated samples is that the curves for all samples except 1D (containing 18.03% Al_2O_3) are convex to the log [g(α)] axis. The curves for sample 1D are concave (Fig. 3) and their significance is not understood at this time.

In the case of mixed samples (Fig. 5), similarly the plots are all curved with comparatively sharp turning points. Clearly the turning points in these samples correspond approximately to the ratios of the two components in the mixtures. From the curves it can be said that the zinc basic carbonate decomposes first with a large slope corresponding to a higher activation energy followed by decomposition of the aluminium hydroxide which is associated with a small activation energy, whatever be the rate equation. In no case can the entire course of reaction be described by a single rate equation. This is interesting since although both pure zinc basic carbonate as well

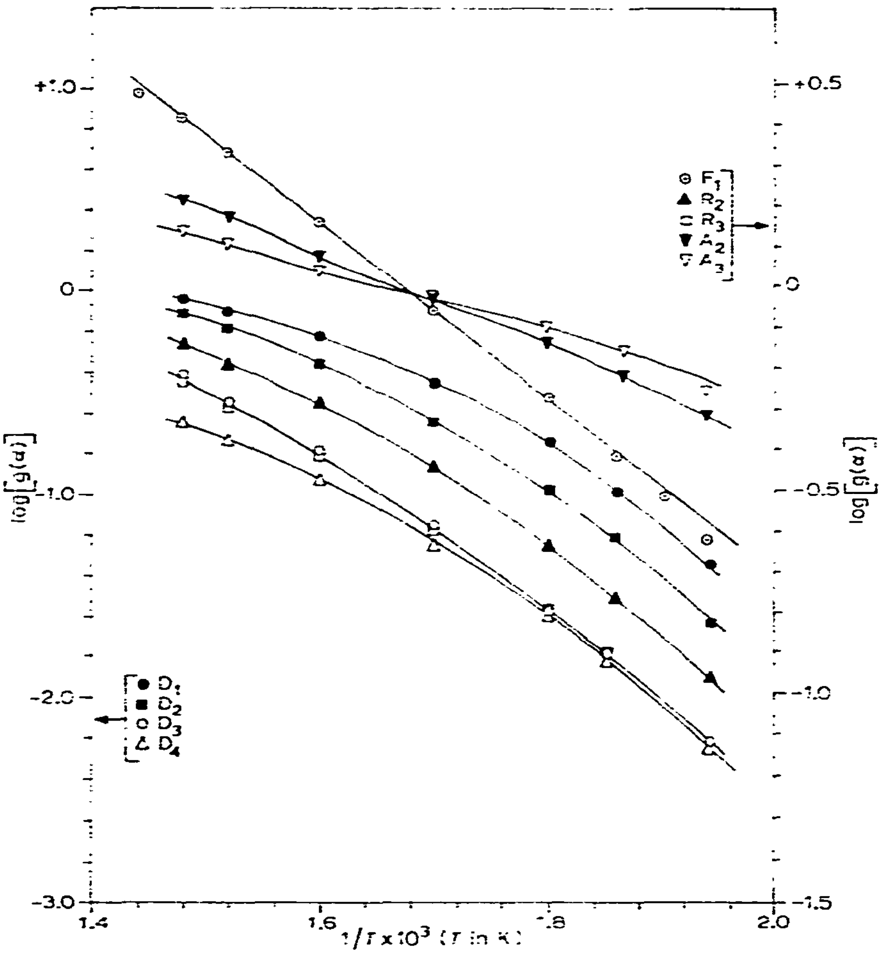

Fig. 2. Šatava's plot for aluminium hydroxide (sample 1B).

as aluminium hydroxide follow first order mechanisms, their mechanical mixtures, like the coprecipitated samples, behave differently.

From the above discussion at this stage the mechanism of decomposition of coprecipitated as well as mixed samples of ZnO–Al_2O_3 system can be visualized as occuring in two distinct steps. The first step is undoubtedly the decomposition of zinc basic carbonate. When a part of the zinc basic carbonate has decomposed, the mechanism perhaps changes and the reaction proceeds with a low activation energy. This change in mechanism may be either due to the presence of ZnO formed in the first step or an interaction between the decomposing species resulting in the formation of "precursor" to spinel, $2ZnO \cdot 3Al_2O_3$.

Šatava^5 has pointed out that the sensitivity of this method is not too high. This may be true for the estimation of the associated activation energy of the process but for the mechanism of reaction, the log [g(x)] plots are supposed to be characteristic. If a straight line is not obtained for the entire course of the reaction using the nine

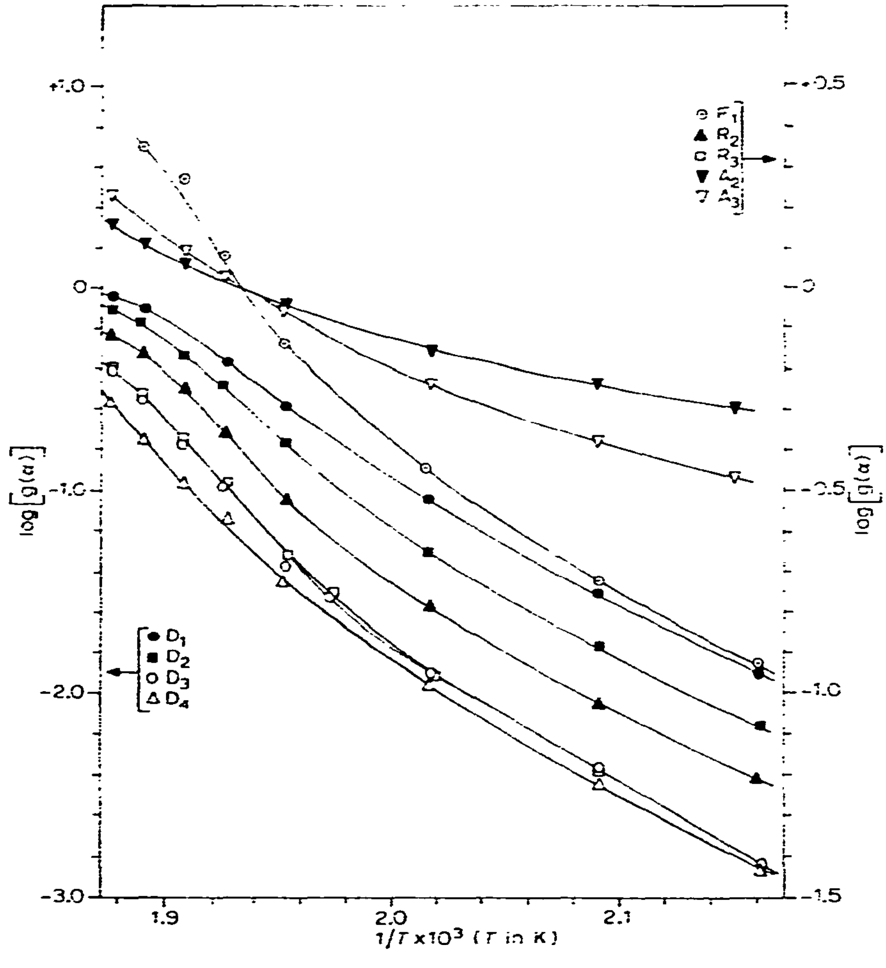

Fig. 3. Šatava's plot for sample 1D.

equations listed in his paper, the only conclusion which can be drawn is that the decomposition reaction is complex in nature.

The decomposition of some of the coprecipitated and mixed samples proceeds through the interaction of the decomposing precipitates, as has been shown in our earlier investigation[1]. If this process is considered as purely a solid state reaction, the Ginstling and Brounshtein equation[5] (D4), Jander equation[5] (D3), Carter[7] and Valensi equation[8], which have fairly wide applicability, should have been applicable in at least some of the samples. But the fact that they are also not applicable rules out the possibility of considering the decomposition of coprecipitated and mixed samples as a purely solid state reaction process, based on these equations. The process is therefore clearly a heterogeneous one with changing mechanism and activation energy during the course of the reaction. There is no such general equation for decomposition reactions which takes into account the heterogeneously proceeding kinetics and mechanism. It appears that the accurate definition of such processes, such as the decomposition of coprecipitated or mixed $ZnO-Al_2O_3$ samples, may lead to several empirical equations for different samples. A necessity therefore exists for a generalized

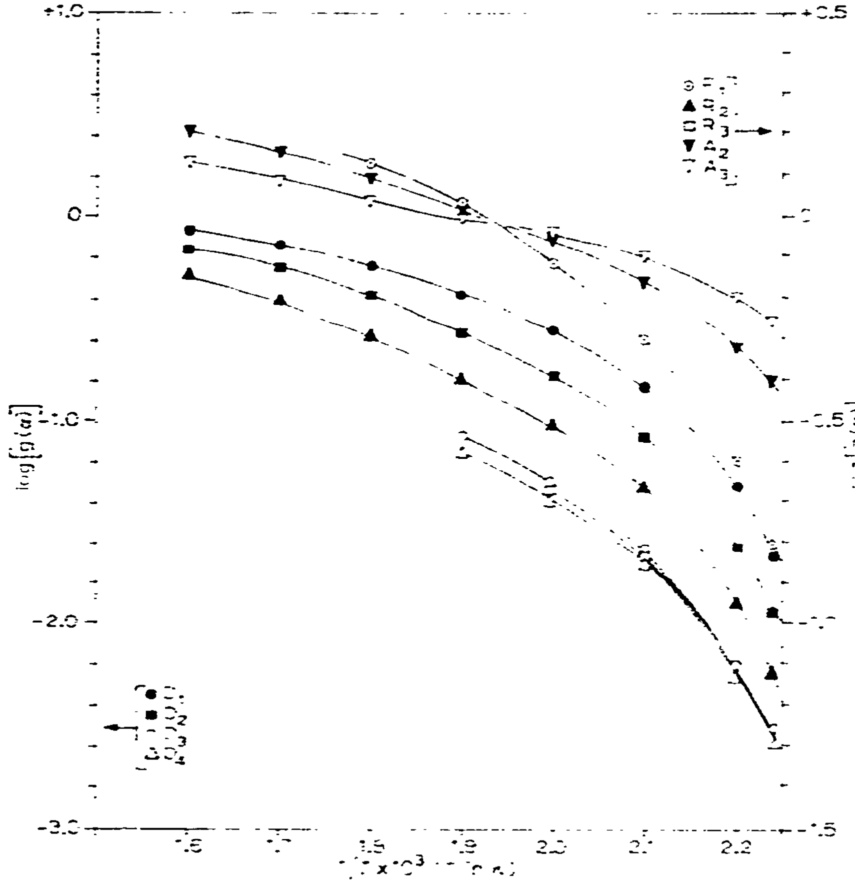

Fig. 4. Šatava's plot for sample 1E.

rate equation which covers the complexities and heterogeneous nature of such decomposition process. It may however be complicated by the fact that there are too many variables to be considered and a mathematical model may be difficult.

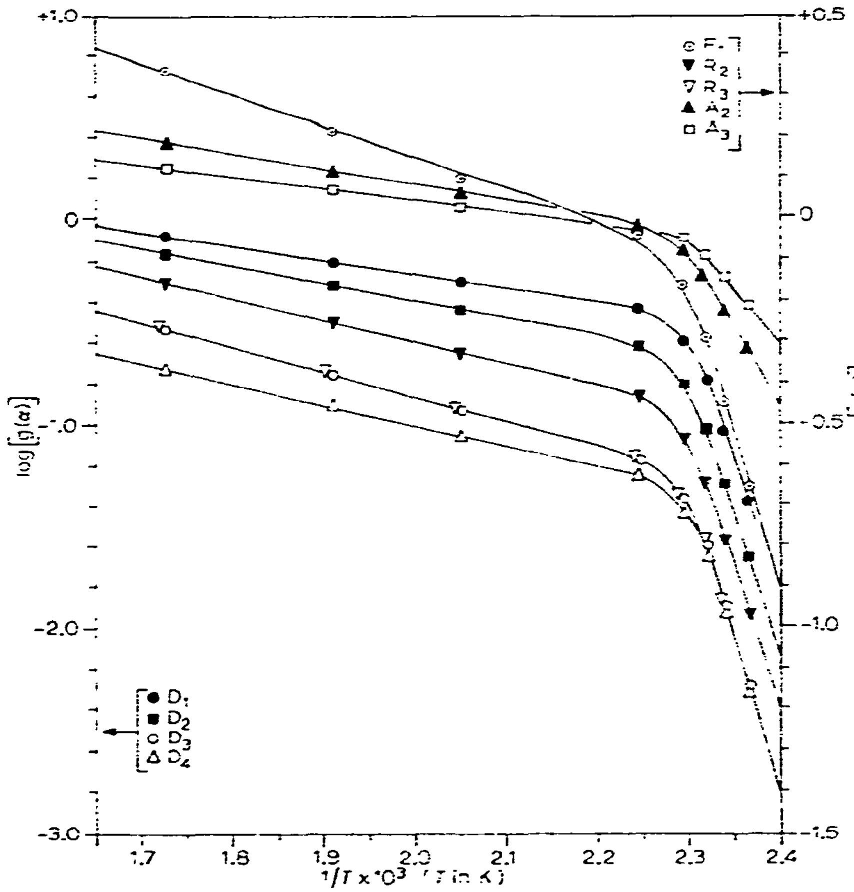

Fig. 5. Šatava's plot for sample 2C.

APPLICATION OF COATS AND REDFERN EQUATION

Šatava's plots in Figs. 1 and 2 for pure zinc basic carbonate (sample 1A) and pure aluminium hydroxide (1B) indicate that the decomposition of the pure precipitate approximates a first order rate process. The Coats and Redfern equation[4] which appears to have been more reliably used when the order of reaction is known, has been applied here to obtain the activation energies for the decomposition of the pure components. It has been also applied to coprecipitated and mixed samples to see if any additional information can be obtained.

The plots, assuming first order kinetics for the pure components, for representative coprecipitated and a mixed sample are shown in Fig. 6. In case of zinc basic carbonate (1A, Fig. 6), the reaction is clearly first order up to 0.96 fraction

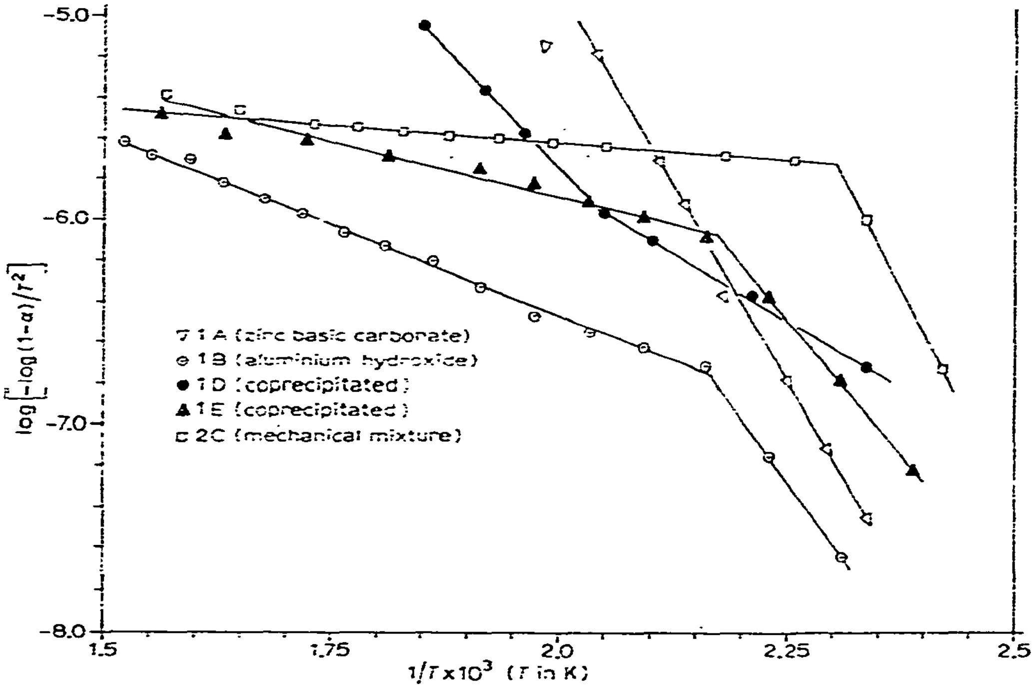

Fig. 6. Coats and Redfern's plot (first order).

decomposition with an activation energy of 34.5 kcal/mole. For aluminium hydroxide (1B) two straight lines are obtained, the activation energy for the first line which corresponds to only 0.06 fraction decomposition is 29.4 kcal/mole and for the major remaining decomposition, the activation energy is 8.3 kcal/mole. Such breaks in the Coats and Redfern plots are of rare occurrence and the significance of changing activation energy may be the same as the break sometimes observed in Arrhenius plots.

For a first order decomposition reaction, Borchardt and Daniels[9] derived the following equation for the rate constants from DTA peaks

$$K = [C_p(\mathrm{d}\Delta T/\mathrm{d}t)+K\Delta T]/[K(A-a)-C_p\Delta T] \qquad (4)$$

which reduces to

$$K = \Delta T/(A-a) \qquad (5)$$

as the quantities $C_p(\mathrm{d}\Delta T/\mathrm{d}t)$ and $C_p\Delta T$ are small. In eqn (5), ΔT = height of the peak at time t, A = total area under DTA curve, and a = area at time t.

The DTA curves for zinc basic carbonate and aluminium hydroxide are given elsewhere[1]. The activation energy has also been calculated from the plots of log K versus $1/T$ (K obtained from eqn 5), which are linear. The values of 31.8 kcal/mole for zinc basic carbonate (single peak in DTA); 24.9 and 10.04 for the two major peaks at 200 and 400°C, respectively, for aluminium hydroxide, compare well with the values obtained from Coats and Redfern plots (Table 1) of TG data.

TABLE 1

ACTIVATION ENERGIES OF DECOMPOSITION OF COPRECIPITATED SAMPLES

Sample no.	*Composition (%)*		*Apparent activation[a] energy from TGA*		*Apparent activation energy from DTA[b]*	
	Al_2O_3	*ZnO*	*Fraction decomposed (α)*	*E_a (kcal/mole)*	*Peak temp. (°C)*	*E_a (kcal/mole)*
1A		99.2	0–0.96	34.5	325	31.8
1B	98.9		0–0.06	29.4	230	36.5
			0.06–1.0	8.3	400	10.04
1C	10.67	89.38	0–0.33	42.0	230	36.5
			0.33–1.0	15.12	385	12.2
1D	18.03	81.97	0–0.23	12.1	250	10.7
			0.23–1.0	28.0	290	21.0
1E	38.82	64.18	0–0.24	25.1	165	21.4
			0.24–0.67	6.38		
			0.67–1.0	2.95	275	9.3
1F	55.98	44.02	0–0.32	19.32	190	16.8
			0.37–0.75	6.3		
			0.75–1.0	2.68	275	6.3
1G	82.93	17.07	0–0.15	24.5	200	21.7
			0.15–1.0	5.3	400 and 500	7.0

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[a] Coats and Redfern equation, assuming first order kinetics. [b] Borchardt and Daniels equation, for first order kinetics.

The Coats and Redfern plots for coprecipitated and mixed samples are all characterized by one or two breaks at different decomposition fractions. The details of the curve breaks and the corresponding activation energies for the decomposition of all the samples are summarized in Table 1. In general the activation energies calculated from DTA peaks compare well with those calculated from the Coats and Redfern plots.

The decomposition of coprecipitated samples is a two step process except in samples 1E and 1F. The initial decomposition (up to 0.2–0.3 fraction) requires higher activation energies in all cases except in sample 1D (18.03% Al_2O_3). In sample 1D, initially the activation energy is lower, which also explains the concave nature of the curve (Fig. 5) in plots of log [$g(\alpha)$] versus $1/T$ for this sample. No obvious reason can be given for this. In samples 1E and 1F the decomposition is a three step process since two breaks have been observed in the Coats and Redfern plots and thus three values for the activation energy have been reported (Table 1). Only in samples 1E and 1F in our earlier investigation have we reported the possibility of partial interaction between the decomposing species resulting in the formation of precursor to spinel, $2ZnO \cdot 3Al_2O_3$. The additional third step appearing in these two samples is at 0.7 fraction decomposition and may correspond to the interaction resulting in formation of precursor. This step is associated with the lowest activation energy (2.5–3.0 kcal/mole).

The activation energies calculated from the Coats and Redfern plots (TGA) and Borchardt and Daniels equation (DTA) for pure aluminium hydroxide (1B) and sample containing 82.93% Al_2O_3 (1G) are of the same order. The identical decomposition behaviour of these two samples confirms our views expressed in our earlier investigation[1] that in sample 1G interaction occurs resulting in formation of precursor mainly during coprecipitation and not during thermal decomposition.

MECHANICAL MIXTURES

The samples follow more or less similar trends, as in the coprecipitated samples, with regard to the number of breaks in the curves and the associated activation energies (Table 2). In general, activation energies of decomposition of mechanically mixed samples are higher than those of corresponding coprecipitated samples. This may be due to poor dispersion of the components in the mixtures and the effect of non-uniform particle size, etc. The activation energy for the first step, which is the decomposition of zinc basic carbonate, is always high and for the second step, *i.e.*, the decomposition of aluminium hydroxide in sample 2A, it is 22.2 kcal/mole and for the remaining samples (2B–2E) it is only in the range of 1–5.0 kcal/mole. For pure aluminium hydroxide, an activation energy of 29.4 and 8.3 kcal/mole has been reported (Table 1). In mechanical mixtures the drastic change in activation energy in the second step may be due to several reasons; a possible one is interaction with zinc

TABLE 2

ACTIVATION ENERGIES OF DECOMPOSITION OF MECHANICALLY MIXED SAMPLES

Sample no.	*Composition (%)*		*Apparent activation energy from TGA*[a]		*Apparent activation energy from DTA*[b]	
	Al_2O_3	ZnO	*Fraction decomposed (x)*	E_a *(kcal/mole)*	*Peak temp. (°C)*	E_a *(kcal/mole)*
2A	8.1	91.9	0–0.6	43.5	260	37.8
			0.6–1.0	22.2		
2B	16.6	83.4	0–0.65	54.9	290	36.5
			0.65–1.0	1.0		4.9
2C	34.6	65.4	0–0.46	32.5	315	34.6
			0.46–0.82	1.4		
			0.82–1.0	4.0		
2D	54.3	45.7	0–0.32	29.57	255	24.0
			0.32–0.6	3.5		5.4
			0.6–1.0	1.6		
2E	76.0	24.0	0–0.22	23.5	275	17.3
			0.22–1.0	5.3	390	7.0

[a] Coats and Redfern equation, assuming first order kinetics. [b] Borchardt and Daniels equation, for first order kinetics.

oxide resulting in the formation of the precursor, which is prominently observed in sample 2C and 2D where two breaks have been observed. In our earlier investigation a possibility of partial interaction has been indicated.

Very low values of activation energies observed in coprecipitated and mechanically mixed samples of the ZnO–Al_2O_3 system during the later stages of decomposition probably correspond to the interaction of the decomposing species, forming the precursor. Such low values may also suggest that formation of the precursor might be occurring through a surface diffusion mechanism.

The justification for considering the decomposition of coprecipitated and mechanically mixed samples as first order rate process and for application of Coats and Redfern equation is one point which remains to be resolved. Under the circumstances, as has been pointed out earlier, in the absence of any other suitable rate equation it may be justified. However, the necessity of a more general rate equation for this type of heterogeneous decomposition process is stressed.

EQUATION FOR HETEROGENEOUS DECOMPOSITION PROCESS—AN APPLICATION OF THE ELOVICH EQUATION TO THE DECOMPOSITION PROCESS

From the foregoing discussion it may be concluded that the attempt to represent kinetics data of coprecipitated and mixed samples by algebraic mass action functions involving integral or fractional powers of concentration or even definite order has not been entirely successful. The Elovich equation[10] has found most general applicability for chemisorption processes and has also been used by many authors for interpretation of results of gas–solid chemical reactions, *e.g.*, reduction[11] and oxidation and reaction of H_2S with supported nickel catalysts[12]. It is argued that though the Elovich equation is empirical, its general applicability is unquestionable and moreover several different approaches to the mechanism of chemisorption have resulted in a logarithmic rate law so that the Elovich equation also can no longer be regarded as a purely empirical formulation. In the solid state decomposition reaction also, several logarithmic rate equations have been derived from theoretical considerations.

It has been indicated earlier that the decomposition of coprecipitated and mixed samples appears to be a heterogeneous process with changing of activation energies. It has also been mentioned[12] that a sum of simultaneously occurring independent first order or second order reactions will approximate Elovich kinetics. The basic premise of the Elovich equation is heterogeneously occurring reactions and breaks in Elovich plots may correspond to Low's theory of multiple kinetic stages[10]. It will be therefore interesting to look into the possibility of application of this equation for the kinetics of decomposition of the samples of the ZnO–Al_2O_3 system.

The Elovich rate law is generally written as

$$\mathrm{d}q/\mathrm{d}t = a \cdot \exp(-bq) \tag{6}$$

where q is amount of gas adsorbed and a and b are empirical constants. Adapting this equation to the decomposition process we have considered α as the fraction decomposed and a and b are retained as constants. Equation (6) may be then rewritten as

$$d\alpha/dt = ae^{-b'\alpha} \tag{7}$$

Since we are dealing with a nonisothermal process, eqn (7) requires transformation according to Šatava's method, thus

$$d\alpha/dt = ae^{-b'\alpha} = a \cdot f(\alpha).$$

Though a is not exactly the rate constant, still $f(\alpha)$ may be approximated and equated to $e^{-b'\alpha}$.

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^{\alpha} e^{b'\alpha} d\alpha = B \cdot e^{b'\alpha} - B \tag{8}$$

where B is a new constant. From eqn (8), the Elovich rate equation now assumes the form

$$B \cdot e^{b'\alpha} - B = Kt$$

$$\text{or } e^{b'\alpha} = K't + 1 \tag{9}$$

Equation (9) is a highly simplified form of Elovich equation in which the rate constant also appears. The applicability of eqn (9) to chemisorption data, which obeys the Elovich rate law, has actually been tested with published experimental data of Low[10] and Narayanan *et al.*[13]. A straight line results in a plot of $e^{b'\alpha}$ versus t with an intercept equal to 1. The b' in this equation can be obtained from an α (or q) versus log t plot as in the original Elovich equation. The further implications of this equation to chemisorption processes will be discussed separately in another communication.

Considering the non-isothermal case, in a plot of $\log[g(\alpha)]$ ($g(\alpha)$ is equal to $Be^{b'\alpha} - B$) versus $1/T$, the nature of the curve will not be affected by B and b' in the term appearing on left-hand side of the minus sign and hence, only B on the right-hand side of the minus sign remains significant in such a plot. Therefore, a plot of $\log(e^{\alpha} - B)$ versus $1/T$ should indicate the applicability of eqn (8) to heterogeneous decomposition processes in a nonisothermal experiment.

The value of B has to be arbitrarily chosen which gives a straight line where the equation applies. The B appears to be a sort of linearizing constant, though it is observed to be more significant, as will be shown later, than the linearizing constant K which is used in the Elovich equation[10].

In the case of the ZnO–Al_2O_3 samples the values of B were found to be negligibly small; the plots of $\log(e^{\alpha})$ versus $1/T$ are shown in Figs. 7–9. The plots for pure zinc basic carbonate and aluminium hydroxide (Fig. 7) are S-shaped and hence eqn (8) does not apply. In Fig. 8 (coprecipitated samples), for the samples containing approximately 10, 18 and 83% Al_2O_3 (1C, 1D and 1G, respectively) the curves are all S-shaped but those containing 39 and 56% Al_2O_3 (1E and 1F) give straight lines with one break. It may be recalled that only in 1E and 1F is the possibility of inter-

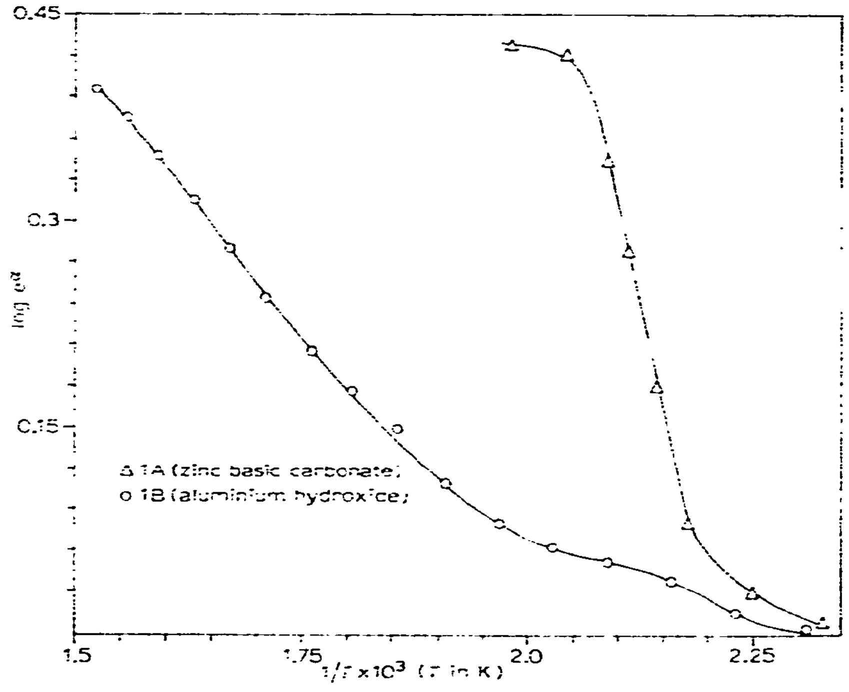

Fig. 7. Curves for pure components.

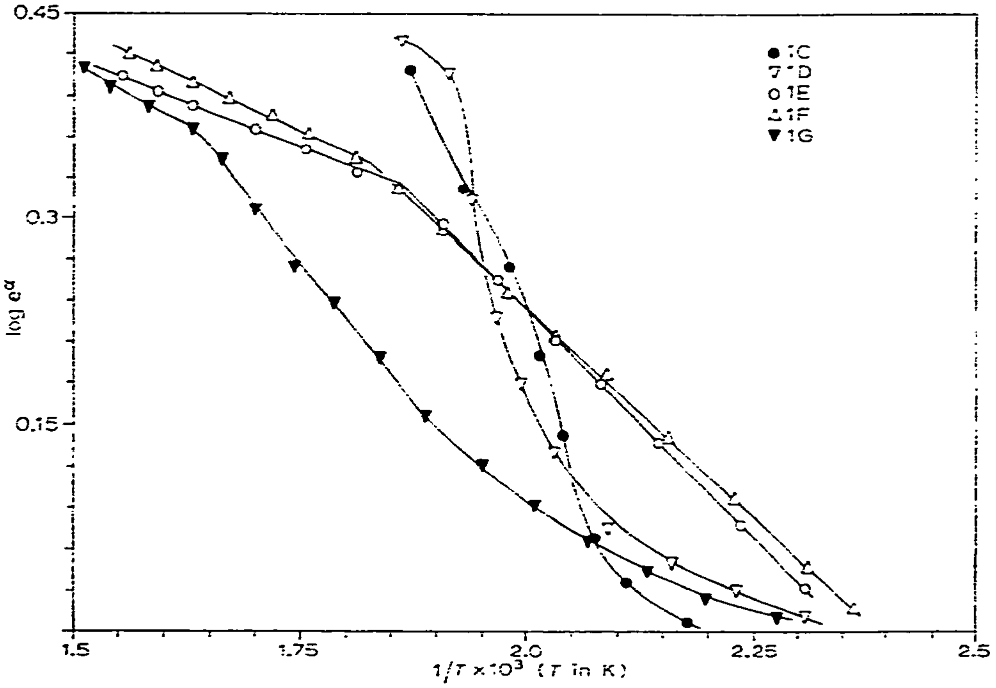

Fig. 8. Curves for coprecipitated samples.

action forming precursor during decomposition suggested[1]. The applicability of the proposed equation only in these two samples is quite significant. In the case of mechanically mixed samples, while samples 2C and 2D give S-shaped curves, the other samples, 2E, 2F and 2G, gives straight lines, as shown in Fig. 9. Once again only in these three samples has precursor formation during decomposition been hinted[1]. In sample 2G the entire course of reaction can be described by a single straight line (Fig. 9), whereas in the Coats and Redfern plot, a break is observed (Fig. 6). The activation energies calculated from these plots (Figs. 8 and 9) by comparison with log p(x) versus 1/T curves[5], give values in the range of 1.0–5.0 kcal/mole for the samples where eqn (8) is applied.

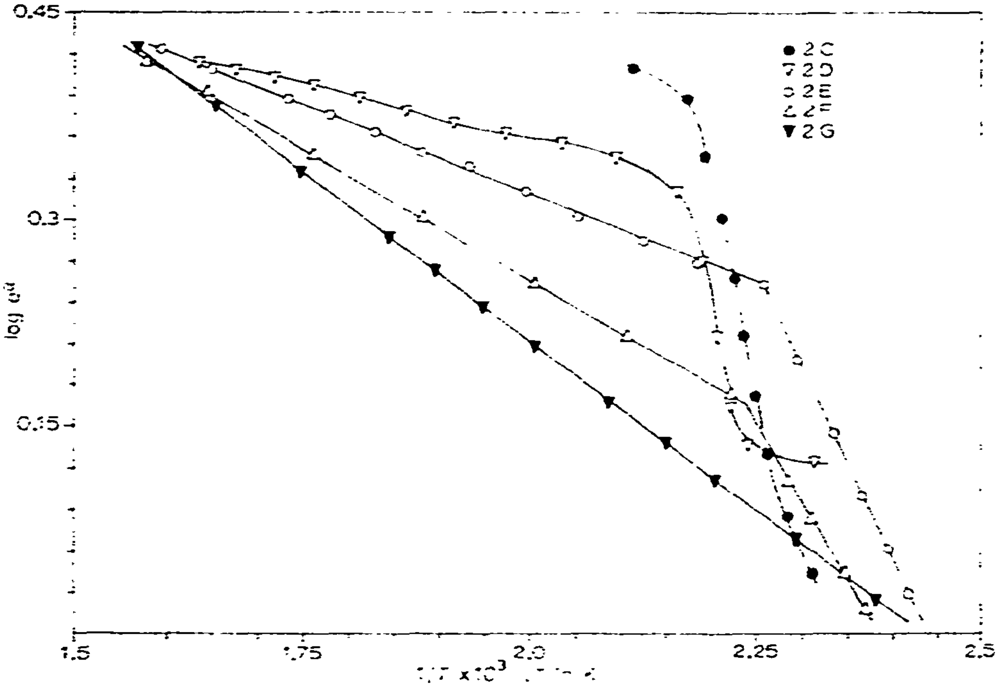

Fig. 9. Curves for mechanically mixed samples.

At this stage we have reason to believe that eqn (8) is probably a general equation applicable to processes which are heterogeneous in the sense that the activation energy changes during the course of the reaction due to some interaction among the decomposing species, as well as to the processes with diffusion as the rate controlling mechanism. This equation therefore should be applicable in the instances where such equations as D_1, D_2, D_3 and D_4 (ref. 5) apply. To illustrate this point theoretically constructed nonisothermal data for D_1–D_4 equations has been plotted according to eqn (8) and are shown in Fig. 10. It can be seen that with a certain specific B value straight lines are obtained in plots of $\log (e^x - B)$ versus $1/T$. The value of B appears to be significant and may be related to the rate controlling process. For D_1 and D_2 the values of B are 1.03 and 1.0, respectively, and for D_3 and D_4 they are

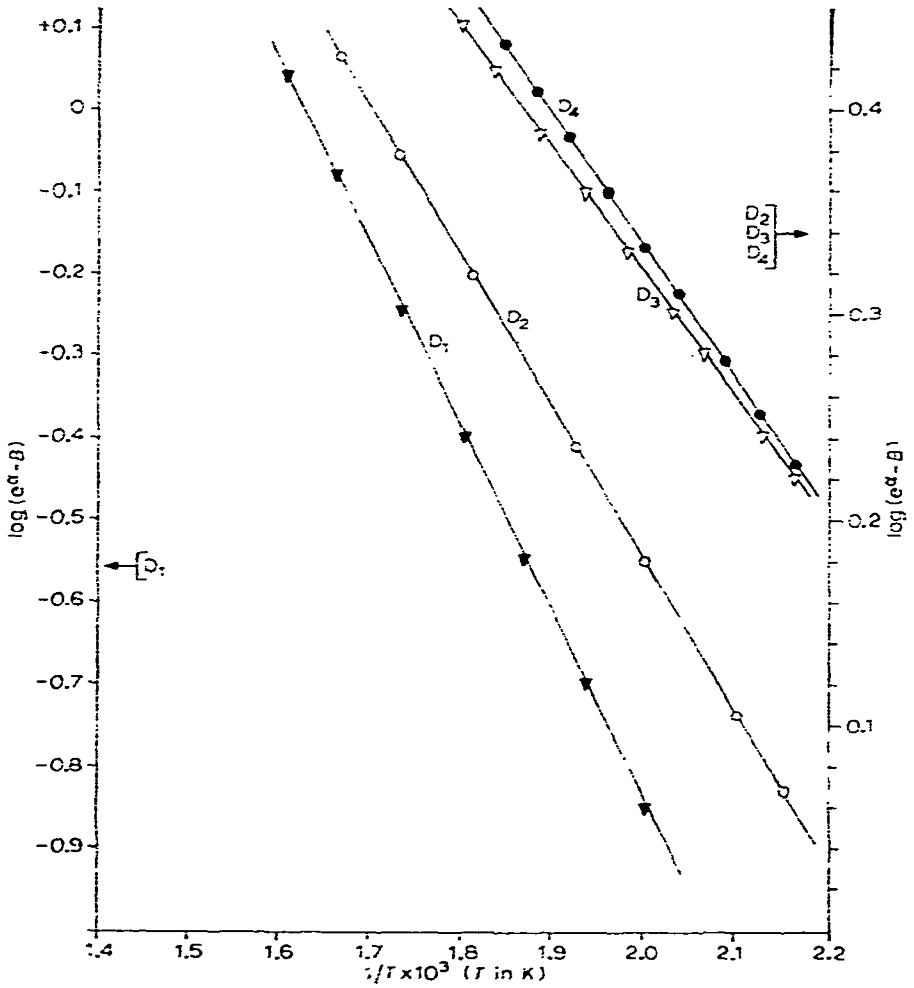

Fig. 10. Plots of diffusion equations.

the same, *i.e.*, 0.97. Incidentally for D_3 and D_4, the rate controlling process is also the same, *i.e.*, three dimensional diffusion and spherical symmetry though the equations are different. This strongly indicates the relation between the constant *B* and the rate controlling process. The very small values of *B* as observed in the $ZnO-Al_2O_3$ samples do not correspond with any of the values of known equations (e.g. D_1-D_4) and such a small value of *B* probably may correspond to a surface diffusional mechanism. Further work is being carried out along these lines to understand the significance of *B* and test the general applicability of eqn (8) to other diffusion controlled and heterogeneous processes.

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